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⑤ Lithium oxide based amorphous material and process for preparation thereof.

⑦ Disclosed is a lithium oxide based amorphous material having a composition included in the region defined by straight lines connecting the points A, B, C and D in the composition diagram of the ternary system $\text{Li}_2\text{O} \cdot \text{SiO}_2 \cdot \text{P}_2\text{O}_5$ forming Fig. 1 of the accompanying drawings. This amorphous material can be formed by sputtering using as a target a mixture of a lithium silicate/lithium phosphate composition and Li_2O . This amorphous material has excellent ionic conductivity.

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LITHIUM OXIDE BASED AMORPHOUS MATERIAL AND
PROCESS FOR PREPARATION THEREOF

The present invention relates to a lithium oxide based amorphous material and a process for the preparation thereof.

Interest in solid lithium ion conductors has recently been increasing, especially, for their use as a solid electrolyte of a lithium cell or an electrolyte of an electrochromic display device. In the former case, since the requirement for reduction of the thickness of the cell has been increasing with recent requirements for minimization of the sizes of electronic devices and reduction of their thickness, the possibilities for application have been abruptly expanded. For example, a lithium cell comprising an evaporated film of LiI as a solid electrolyte is proposed in J. Electro. Chem. Soc., vol. 116, No. 10, page 1452 (1969). This evaporated film, however, consists of a polycrystalline body having a thickness of about 10 to about 15 μm , and the ionic conductivity of the film is about $10^{-7} \text{ mho}\cdot\text{cm}^{-1}$.

In electrochromic display devices, the solid electrolyte is used to render the device totally solid

and to stabilize the structure of the device.

In both the cases, it has been sought to develop a solid electrolyte which has a high ionic conductivity and is stable in the ordinary atmosphere. At present, however, since resistance to ionic conduction in the solid electrolyte is high, no satisfactory devices of the above mentioned types have in practice been developed.

To increase the ionic conductivity of the above-mentioned device, there can be considered a method in which the solid electrolyte is formed into a thin film so as to reduce resistance geometrically. By conventional ceramic techniques, however, it is difficult to form a thin film of thickness less than 10 μm . Furthermore, by conventional film-forming techniques such as the CVD method or the sputtering method, a thin film having a high ionic conductivity cannot be obtained. The reason for this is that the temperature for the synthesis of an oxide based solid electrolyte is high, so that an alkali metal oxide is lost by evaporation or the like during formation of a thin film and control of the composition is therefore difficult.

The following reference is cited to show the state

of the art: J. Electro. Chem. Soc., vol. 124, No. 8, page 1240 (1977).

It is a primary object of the present invention to provide a lithium oxide based amorphous material which can have an excellent ionic conductivity.

Preferably, the material can be formed as a thin film.

The present invention is set out in the claims.

The invention will now be further explained, and embodiments described by way of example, with reference to the accompanying drawings, in which:-

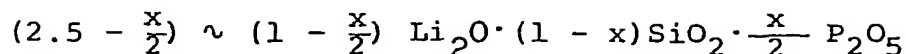
Fig. 1 is a composition diagram of the ternary system of $\text{Li}_2\text{O}:\text{SiO}_2\cdot\text{P}_2\text{O}_5$.

Figs. 2, 3 and 4 are graphs showing the temperature dependency of the ionic conductivity, which are given for illustrating the present invention.

The region defined by straight lines connecting points A, B, C and D to one another in the ternary system composition diagram of Fig. 1 is a region represented by

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the following formula:



From the results of the electron beam diffractometry and X-ray diffractometry of thin films obtained in Examples given hereinafter, it has been confirmed that solid solutions having a composition represented by the above formula are amorphous.

These films have excellent ionic conductivity. From the viewpoint of the ionic conductivity, it is preferred that the amorphous material of the present invention should have a composition included in the region defined by lines connecting points E, F, G and H in Fig. 1, especially by lines connecting points E, I, J and H in Fig. 1.

As a material having a composition included within the above-mentioned region, there is known a polycrystalline body having a composition of, for example, $(1 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_3\text{PO}_4$. However, since this body is a sintered body, only a product having a thickness of several millimeters is obtained and the resistance of this sintered body is very high. Accordingly, this sintered body cannot be used as a lithium ion conductor in the above-mentioned devices.

The amorphous material of the present invention can be obtained in the form of a thin film having a thickness

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of 0.1 to 50 μm , preferably about 1 to about 20 μm , and therefore, the resistance is low. Accordingly, the amorphous material of the present invention can be effectively used as a lithium ion conductor of the above-mentioned devices.

The amorphous material of the present invention can be prepared according to the sputtering method by using as the target a mixture comprising (1) a lithium silicate/lithium phosphate composition represented by the general formula $(1 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_3\text{PO}_4$ wherein x is a value in the range of $0.05 \leq x \leq 0.95$ or a mixture capable of forming said lithium silicate/lithium phosphate composition by sputtering and (2) a lithium compound capable of forming Li_2O on sputtering, for example, Li_2O itself or Li_2CO_3 .

The above general formula $(1 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_3\text{PO}_4$ can be rewritten as $(2 - \frac{x}{2})\text{Li}_2\text{O} \cdot (1 - x)\text{SiO}_2 \cdot \frac{x}{2}\text{P}_2\text{O}_5$, and it indicates a composition shown by the broken line h in the ternary system composition diagram of Fig. 1. If only the lithium silicate/lithium phosphate composition is used as the target without mixing of Li_2O or the like and sputtering is carried out, the resulting composition is one formed by removing Li_2O from the starting material composition, that is, $(1 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_3\text{PO}_4 - n\text{Li}_2\text{O}$. On the other hand, if Li_2O is added to the above

starting material according to the present invention and sputtering is carried out, a product having a composition corresponding substantially to the above general formula $(1 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_3\text{PO}_4$ can be obtained. If the amount incorporated of Li_2O or the like is increased, a product having a composition in which the content of Li_2O is higher than in the composition of the above general formula can be obtained.

More specifically, if the ratio of lithium silicate/lithium phosphate of the starting material, that is, the value of x , is determined, the corresponding position in the composition diagram of Fig. 1 should naturally be determined. In short, a corresponding point on the dotted line h is determined. Supposing that x is 0.40, the composition corresponds to the crossing point of the dotted lines h and c. If sputtering is carried out by using the starting material having this composition as the target, as pointed out hereinbefore, the resulting product has a composition formed by removing Li_2O from the composition of the starting material, that is, a composition on the dotted line c or an extension thereof, which is below the crossing point of the dotted lines h and c and is very close to the line of $\text{Li}_2\text{O} = 0$. If a mixture of the above composition and Li_2O is used as the target, the product has a composition on the

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dotted line c or an extension thereof and is located at a higher position (on the side of Li_2O) with increase of the proportion of Li_2O .

For example, if 1 mole (per mole of the starting composition; the same will hold good hereinafter) of Li_2O is mixed, the product obtained has a composition at point 7. If the amount of Li_2O to be mixed is increased to 2, 3, 4, 5 or 7 moles, the product comes to have a composition at point 3, 8, 9, 10 or 11 on the dotted line c.

If the amount added of Li_2O is further increased, a product having a composition in which the proportion of Li_2O is increased, for example, a composition located above a line connecting points A and D in Fig. 1 (on the side of Li_2O), is obtained. This composition, however, is not preferred from the viewpoint of the ionic conductivity. Accordingly, it is preferred that sputtering be carried out by using Li_2O in an amount of up to 8 moles.

Also a product having a composition having too small an amount of Li_2O , for example, a composition below the line B-C in Fig. 1 (located below the line B-C in Fig. 1), is inferior in ionic conductivity. Therefore, it is preferred that the amount of Li_2O to be mixed be at least 1.5 moles, especially at least 1.8 moles.

It is preferred that the lithium silicate/lithium

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phosphate composition to be used as the target be a lithium silicate/lithium phosphate solid solution formed by ball-milling the starting materials and sintering them to effect solid phase reaction. The reason is that since the ratio of P_2O_5 and Si_2O can be kept constant in the product, namely since the product has, for example, a composition on the dotted line c in Fig. 1 or an extension thereof, by determining only the amount of Li_2O , a solid solution having a desired composition can easily be obtained. When the starting composition is used in the form other than such solid solution, it sometimes happens that the composition of the product deviates from the dotted line c. Incidentally, the dotted lines a, b, c, d, e, f and g in Fig. 1 indicate compositions of products obtained when the values of x are 0.05, 0.20, 0.40, 0.50, 0.60, 0.80 and 0.95, respectively. If the value of x is smaller than 0.05 or larger than 0.95, no good ionic conductivity can be obtained.

As pointed out hereinbefore, a lithium compound capable of forming Li_2O by sputtering can be used instead of Li_2O . However, compounds containing elements reactive with the product as elements other than lithium and oxygen, such as halogens, are not preferred. Accordingly, in the present invention, it is preferred that at least

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one compound selected from the group consisting of Li_2O , Li_2CO_3 and LiOH be used.

It is preferred that such compound be used in an amount of 3 to 16 moles as the lithium atom per mole of the composition, namely 1.5 to 8 moles as the Li_2O compound as pointed out hereinbefore.

The mixture of the lithium silicate/lithium phosphate composition and the lithium compound may be used in the form of a powder formed merely by mixing the two components or after molding and sintering of such powder.

The present invention will now be described in detail with reference to the following Examples that by no means limit the scope of the invention.

Examples 1 through 6

Starting powders of SiO_2 , Li_2CO_3 and Li_3PO_4 were weighed and mixed so that the ratio of Li, Si and P corresponded to $(1 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_3\text{PO}_4$ in which x was 0.05, and the mixture was reacted at 1000°C for 3 hours to obtain a composition represented by the above formula.

Similarly, the respective starting powders were weighed and mixed so that the ratio of Li, Si and P corresponded to $(1 - x)\text{Li}_4\text{SiO}_4 \cdot x\text{Li}_3\text{PO}_4$ in which x was 0.2, 0.4, 0.5, 0.6 and 0.95, and the mixtures were reacted at 1000°C for 3 hours to obtain compositions of the above formula in which x indicated the above-mentioned values.

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Each so-formed composition was mixed with Li_2CO_3 in an amount of 2 moles per mole of the composition, and the mixture was sintered again at 1100°C . A thin film was prepared according to the sputter-up method by using the sintered product as the target. More specifically, sputtering was carried out under a degree of vacuum of 2×10^{-2} mm Hg at a plate voltage of 2 KV and a deposition rate of $0.5 \mu\text{m/hr}$ with a discharge gas of Ar/O_2 (60/40) to form a thin film having a thickness of about $2 \mu\text{m}$ on a quartz glass substrate, while the substrate was being cooled with water to prevent elevation of the substrate temperature.

From the results of the wet chemical analysis of the so-obtained thin films obtained by using as the target the composition in which x was 0.05, 0.2, 0.4, 0.5, 0.6 or 0.95, it was found that the thin films had compositions corresponding to points 1, 2, 3, 4, 5 and 6, respectively, in Fig. 1. For example, the point 2 indicates a composition of $0.56\text{Li}_2\text{O} \cdot 0.39\text{SiO}_2 \cdot 0.05\text{P}_2\text{O}_5$.

The ionic conductivities (at room temperature) of these thin films determined according to the AC measurement method using a blocking electrode are shown in Table 1, and the temperature dependencies thereof are shown in Fig. 2 in which lines 1', 2', 3', 4', 5' and 6' indicate the ionic conductivities of the thin

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films having compositions at the points 1, 2, 3, 4, 5 and 6, respectively, in Fig. 1.

The thin film of the present invention can have an ionic conductivity lower by about one order than that of a ceramic body (sintered body) prepared by the conventional process, even though the thin film of the present invention is amorphous.

Table 1

<u>Example No.</u>	<u>Value x</u>	<u>Ionic Conductivity (mho·cm⁻¹)</u>
1	0.05	$<10^{-10}$
2	0.2	1×10^{-9}
3	0.4	4×10^{-8}
4	0.5	3.2×10^{-8}
5	0.6	5×10^{-10}
6	0.95	$<10^{-10}$

Examples 7 through 11

A composition in which x was 0.4, that is, a composition represented by the formula $0.6\text{Li}_4\text{SiO}_4 \cdot 0.4\text{Li}_3\text{PO}_4$, was prepared according to the same method as described in Examples 1 through 6.

LiO_2 was added in amounts shown in Table 2 per mole of the composition so-obtained and in the same manner as described in Examples 1 through 6, the mixtures were formed into targets and thin films were prepared. The position numbers of the compositions of the obtained

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thin films in Fig. 1 and the ionic conductivities (at room temperature) of the thin films determined in the same manner as described in Examples 1 through 6 are shown in Table 2. The temperature dependencies of the ionic conductivities are shown in Fig. 3, in which lines 7', 8', 9', 10' and 11' indicate the characteristics of the thin films obtained in Examples 7, 8, 9, 10 and 11, respectively, and the line 3' indicates the characteristic at the point 3 for the purpose of comparison.

Table 2

Example No.	Amount (moles per mole of starting composition) of Li_2O	Position Number of Composition	Ionic Conductivity ($\text{mho}\cdot\text{cm}^{-1}$)
7	1	7	$< 10^{-10}$
8	3	8	4×10^{-7}
9	4	9	1.5×10^{-6}
10	5	10	1.7×10^{-6}
11	7	11	8.7×10^{-7}

Examples 12 through 19

The same lithium silicate/lithium phosphate compositions as used in Examples 2, 4 and 5 and compositions where the mixing ratio of the starting materials was changed and the value x was adjusted to 0.8 were synthesized, and they were mixed with Li_2O

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in various amounts. The mixtures were treated in the same manner as described in Examples 1 through 6 to obtain films having compositions corresponding to position numbers of 12 through 19 in Fig. 1. The position numbers in Fig. 1 correspond to the Example numbers. More specifically, the thin films obtained in Examples 12, 15, 16 and 18 had compositions of $0.69\text{Li}_2\text{O} \cdot 0.28\text{SiO}_2 \cdot 0.03\text{P}_2\text{O}_5$, $0.74\text{Li}_2\text{O} \cdot 0.09\text{SiO}_2 \cdot 0.17\text{P}_2\text{O}_5$, $0.59\text{Li}_2\text{O} \cdot 0.14\text{SiO}_2 \cdot 0.27\text{P}_2\text{O}_5$ and $0.78\text{Li}_2\text{O} \cdot 0.07\text{SiO}_2 \cdot 0.15\text{P}_2\text{O}_5$, respectively.

The ionic conductivities of the so-obtained thin films (at room temperature) are shown in Table 3.

Table 3		
Example No.	Amount (moles per mole of starting mixture) of Li_2O	Ionic Conductivity ($\text{mho} \cdot \text{cm}^{-1}$)
12	5	2×10^{-7}
13	5	1.6×10^{-6}
14	5	5.5×10^{-7}
15	5	8×10^{-9}
16	2	1×10^{-10}
17	1.4	$< 10^{-10}$
18	8	4×10^{-9}
19	8	7×10^{-8}

Example 20

Sputtering was carried out by using as the target the same mixture of $0.6\text{Li}_4\text{SiO}_4 \cdot 0.4\text{Li}_3\text{PO}_4$ and $5\text{Li}_2\text{O}$ as used in Example 10, while the substrate holder was cooled

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by liquid nitrogen so as to maintain the substrate temperature below -20°C during the sputtering step. The composition of the obtained thin film was the same as that of the thin film obtained in Example 10, but the ionic conductivity ($20'$ in Fig. 4) of the thin film obtained in this Example was excellent over that ($10'$ in Fig. 4) of the thin film obtained in Example 10.

As will readily be understood from the foregoing description, according to the present invention, a thin film having a much higher ionic conductivity can be obtained even if the thickness is smaller than $5\text{ }\mu\text{m}$. Since the thickness of the thin film according to the present invention is about $1/1000$ of that of a bulk material, and therefore, the resistance of the device to conduction of ions can be reduced to about $1/1000$. Accordingly, it is expected that prominent effects can be attained when the thin film is used as a solid electrolyte for various devices. Furthermore, although the thin film of the present invention is amorphous, it can have ionic conductivity comparable to that of the crystalline body, and therefore, the thin film need not be crystallized by a heat treatment after sputtering. It is expected that the thin film of the present invention will be very valuable as a material for various electronic devices.

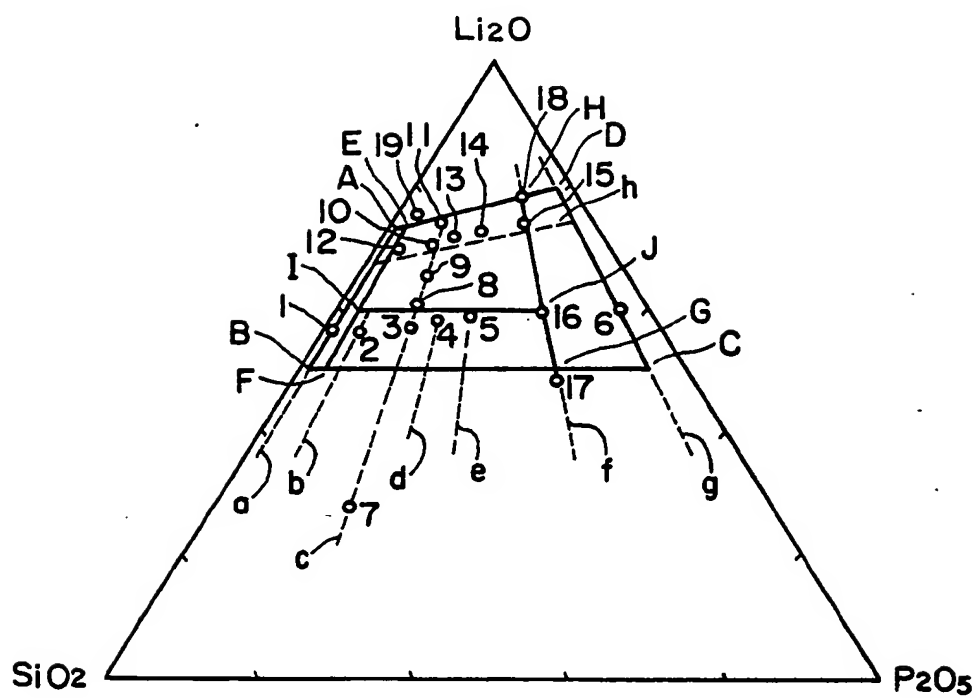
CLAIMS:-

1. A lithium oxide based amorphous material characterised in that it has a composition included in the region defined by straight lines connecting the points A, B C and D in the composition diagram of the ternary system $\text{Li}_2\text{O}.\text{SiO}_2.\text{P}_2\text{O}_5$ forming Fig. 1 of the accompanying drawings.
2. A material according to claim 1, of which the composition is included in the region defined by straight lines connecting the points E, F,G and H in said composition diagram.
3. A material according to claim 1, of which the composition is included in the region defined by straight lines connecting the points E, I, J and H in said composition diagram.
4. A material according to any one of claims 1 to 3, formed in a body having a thickness in the range 0.1 to 50 μm .
5. A process for the preparation of a material according to any one of claims 1 to 4, which comprises sputtering using as a target a mixture comprising the components (a) a lithium silicate/lithium phosphate composition having the general formula
$$(1 - x) \text{Li}_4\text{SiO}_4.x\text{Li}_3\text{PO}_4 \quad - \text{(I)}$$
where $0.05 \leq x \leq 0.95$ or a mixture capable of forming such a lithium silicate/lithium phosphate composition on sputtering and (b) Li_2O or a compound capable of forming Li_2O on sputtering.

6. A process according to claim 5, wherein the lithium silicate/lithium phosphate composition is a solid solution.
7. A process according to claim 5 or claim 6, wherein the component (b) is present in an amount of 3 to 16 moles of lithium atoms per mole of the lithium silicate/lithium phosphate composition.
8. A process according to any one of claims 5 to 7, wherein the component (b) is at least one of Li_2O , Li_2CO_3 and LiOH .
9. A process according to claim 8, wherein component (b) is Li_2O .
10. A process according to claim 8, wherein component (b) is Li_2CO_3 .
11. A process according to any one of claims 5 through 10, wherein x in the general formula (I) is given by $0.10 \leq x \leq 0.80$, and the material prepared has a composition included in the region defined by straight lines connecting the points E, F, G and H in said composition diagram of the ternary system $\text{Li}_2\text{O} \cdot \text{SiO}_2 \cdot \text{P}_2\text{O}_5$.

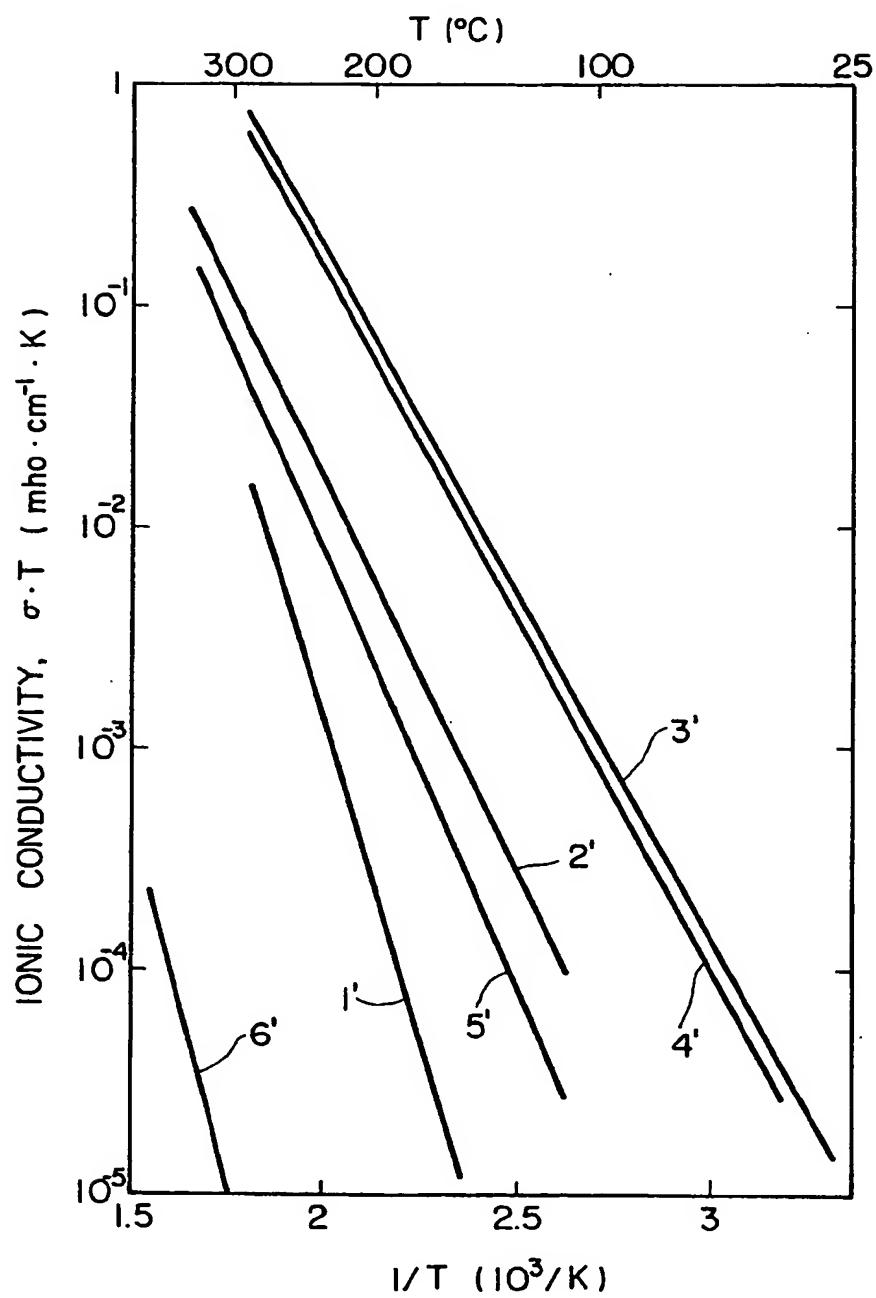
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FIG. 1



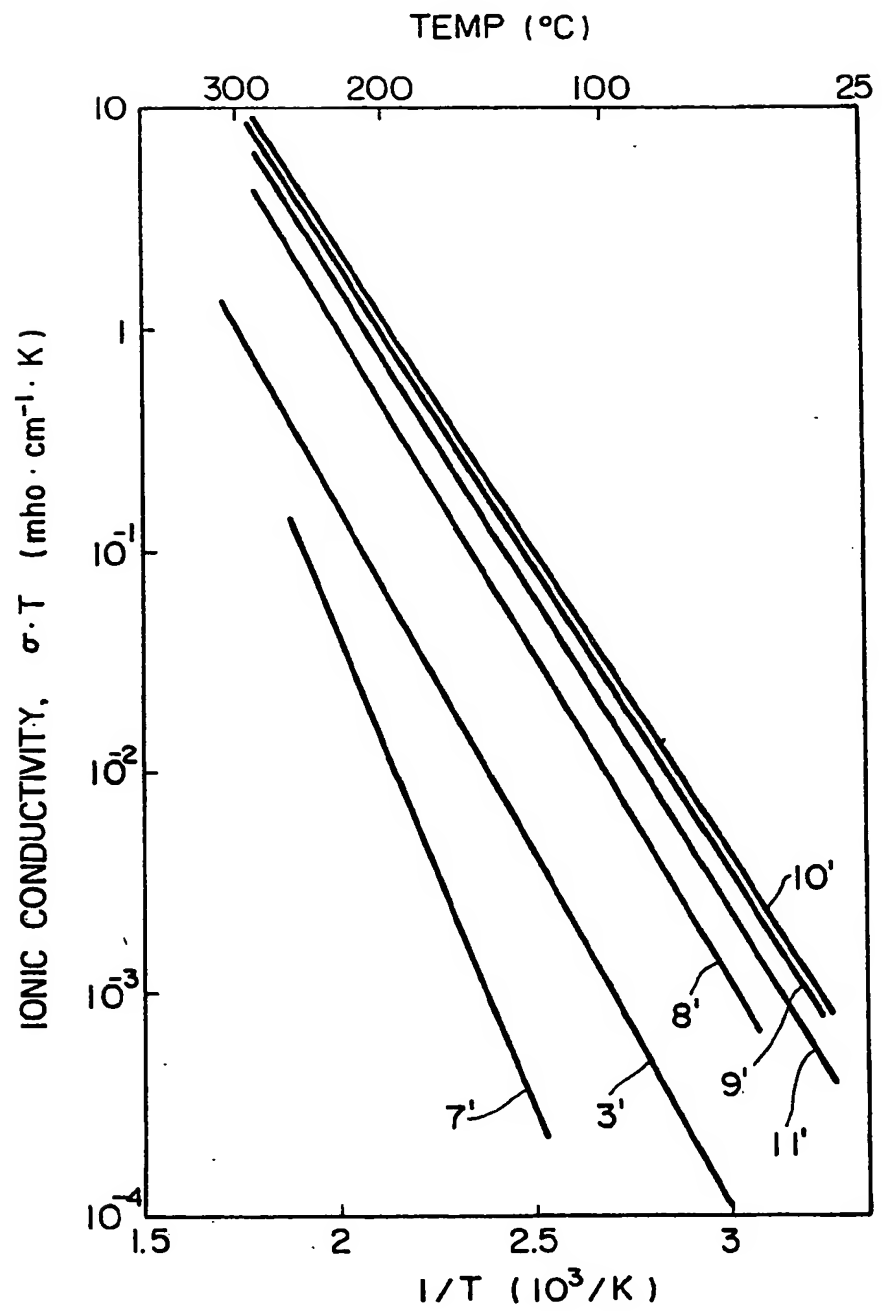
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FIG. 2



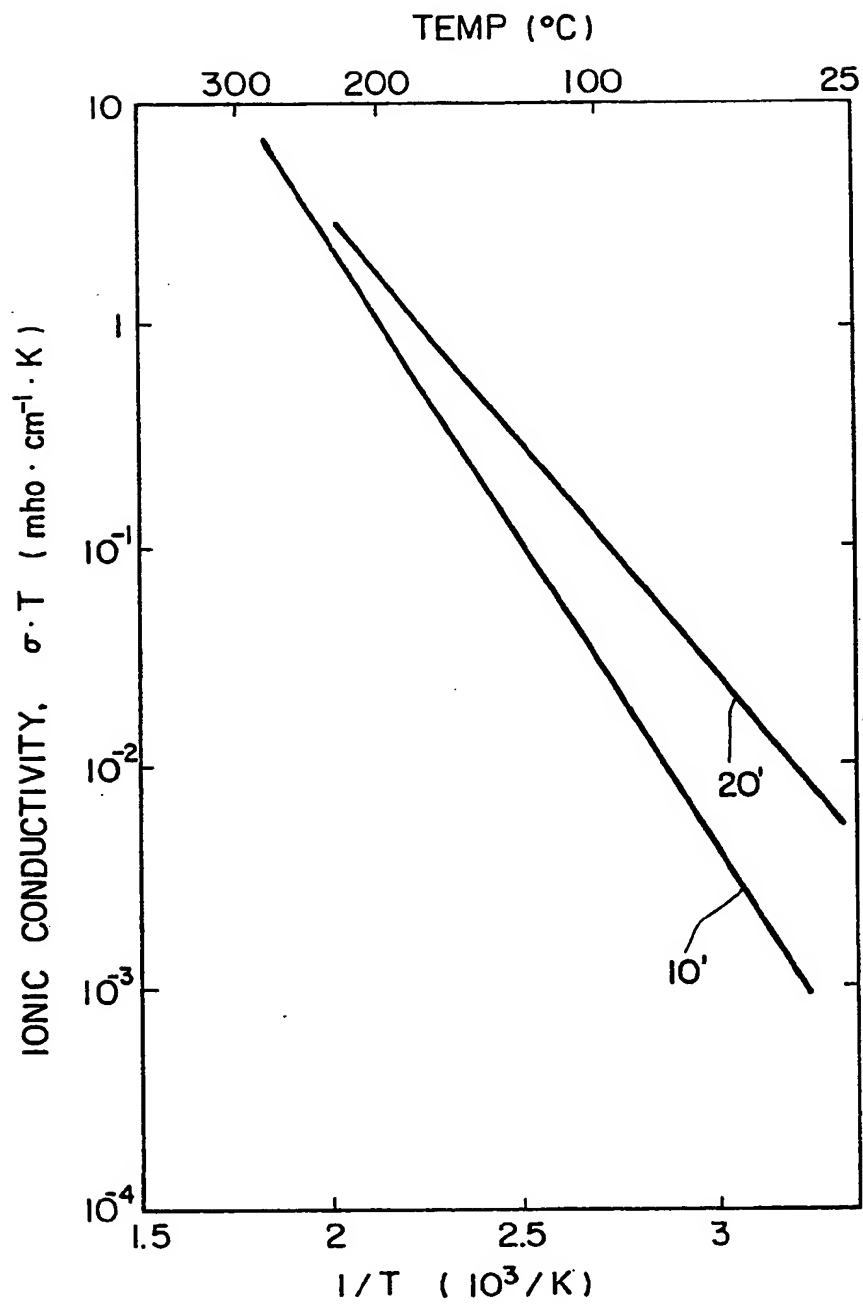
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FIG. 3



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FIG. 4





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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p>GB - A - 2 032 128 (TOKYO SHIBAURA DENKI)</p> <p>* claim 1 *</p> <p>--</p>	1	H 01 M 6/18 G 02 F 1/17 C 03 C 3/30
A,D	<p>J. ELECTROCHEM. SOC., Vol. 124, No. 8, 1977</p> <p>Princeton</p> <p>Y.W. HU et al. "Ionic Conductivity of Lithium Orthosilicate-Lithium Phosphate Solid Solutions"</p> <p>pages 1240 to 1242</p> <p>--</p>		TECHNICAL FIELDS SEARCHED (Int. Cl.3)
A	<p>Chemical Abstracts vol. 85, no. 26, 27 December 1976</p> <p>Columbus, Ohio, USA</p> <p>Y.W. HU et al. " Ionic conductivity of lithium phosphate-doped lithium orthosilicate"</p> <p>page 548, column 2, abstract no. 200928a</p> <p>& Mater. Res. Bull., vol. 11, no. 10, 1976, pages 1227 to 1230</p> <p>--</p>		C 01 B 25/00 C 01 B 33/00 C 01 D 15/00 C 03 C 3/00 G 02 F 1/00 H 01 M 4/00 H 01 M 6/00
A	<p>US - A - 4 184 015 (J.-M. REAU et al.)</p> <p>--</p> <p>./..</p>		CATEGORY OF CITED DOCUMENTS
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
Place of search Berlin			Date of completion of the search 09-11-1981
Examiner KESTEN			



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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	APPLIED PHYSICS LETTERS, Vol. 35, No. 10, 1979, New York L.M. SCHIAVONE et al. "Electrochromic iridium oxide films prepared by reactive sputtering" pages 823 to 825 -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.)

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